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Characterization and testing of $Pt/TiO_2/SiC$ thin film layered structure for gas sensing

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ABSTRACT

This paper presents the results of our investigations on the gas sensing performance of $Pt/TiO_2/SiC$ based field effect devices. The current–voltage characteristics of these $Pt/TiO_2/SiC$ sensors at 530 °C showed a clear shift to lower voltages upon exposure to increasing hydrogen gas concentration. This indicates a reduction in the metal-oxide interface barrier height, arising from the flattening of the energy bands at the interface and can be attributed to the lowering of the Pt work function due to absorption of hydrogen. The effective change in barrier height $\Delta\varphi_b$ for 1% hydrogen in air was found to be 125 meV. The thermal stability of the interfaces in the $Pt/TiO_2/SiC$ devices was studied by Rutherford backscattering spectrometry (RBS). The RBS spectra of the sample in as deposited and annealed conditions were compared and analyzed. The Pt/TiO_2 and TiO_2/SiC layers showed a sharp interface with minimal inter-diffusion. The film composition found to be stable even after repeated testing by exposing to analyte gases. This was further confirmed by X-ray photoelectron spectroscopy analysis of the samples.

1. Introduction

Direct monitoring and control of combustion-related processes that incorporate hydrogen and hydrocarbon gases require sensors in order for them to operate reliably over extended periods, particularly where temperatures may exceed 500 °C [1,2]. Catalytic metal-semiconductor structures fabricated on SiC are the most promising for such applications. Incorporating a reactive metal oxide layers instead of the conventional SiO_2 insulating layer in-between the thin catalytic metal (Pt or Pd) and the SiC substrate has been an area of continued investigation [3–6]. The application of the reactive semiconducting metal oxide layer is targeted towards increasing the sensitivity, selectivity and stability of the sensor towards the analyte gas. One such reactive semiconducting metal oxide is titanium dioxide (TiO_2), which has been widely reported for use in gas sensing applications and is known to be stable at high temperatures [7–9]. To date, numerous other materials have been investigated as the interfacial sensing layer in SiC based field effect hydrogen and hydrocarbon sensors, among them are SnO_2 [10], CeO_2 [11], Ga_2O_3-ZnO [12], Ga_2O_3 [13], WO_3 [14,15], and CoO_x [16].

Nakagomi et al. earlier investigated the use of non-stoichiometric titania in the form of a metal-semiconductor structure on a SiC substrate using the configuration $Pt/TiO_x/SiC$, where they found that a large voltage response of up to 3 V could be obtained by switching the ambient from one containing very high concentrations of H_2 gas to one completely devoid of hydrogen and saturated with O_2. Their results were explained in terms of a simple model consisting of a resistance and Schottky diode connected in series. The response variation in this case was attributed to a change in both barrier height and series resistance; with the change in series resistance resulting from a change in electrical properties of the TiO_x layer under exposure to hydrogen [17]. We also demonstrated the gas sensing performance of a similar $Pt/TiO_2/SiC$ device utilizing stoichiometric TiO_2 not only towards controlled doses of hydrogen in oxygen containing ambient, but also towards propene gas [18]. More recently, Shafiei et al., investigated the effects of anodizing the TiO_2 layer in such devices [19].

Although the underlying operation principles behind these devices are same, the physicochemical reactions occurring at the interface still remain unresolved. For reliable long-term high temperature operation

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of these devices, the thermal stability of different layers and their interfaces becomes a critical requirement for their successive sensor deployment. The changes in the composition due to the inter-diffusion between the layers can affect the Schottky barrier height of the device and potentially lead to the degradation of the sensor characteristics. Consequently, the objective of this work is to analyze the film composition and understand the interfacial diffusion effects between $Pt/TiO_2/SiC$ sensors using X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS). In order to evaluate the long term stability of the proposed devices, the interfaces (Pt/oxide & oxide/SiC) in different conditions, which include as-deposited, annealed (thermal treatment at 650 °C in air) and tested (exposed to O_2, H_2 and C_3H_6 at 650 °C) have been compared and analyzed.

2. Experimental details

The $Pt/TiO_2/SiC$ devices were fabricated on nitrogen-doped ($1.56 \times 10^{18}/cm^3$) n-type 6H-SiC wafers (Dow Corning, USA). An ohmic contact was formed on the unpolished side of the wafer. The contact layers consist of 100 nm thick Ti and 100 nm thick Pt, which were deposited using D.C. sputtering. On the polished side of the wafer the TiO_2 layer was deposited by R. F. sputtering, to a thickness of 100 nm. The TiO_2 film was deposited at a substrate temperature of 300 °C, with an applied RF power of 50 W and working pressure of 0.13 Pa (50% Ar + 50% O_2), resulting in a deposition rate of 5 nm/min [20]. A Pt pad of approximately 1 mm in diameter and 100 nm in thickness was deposited on to the TiO_2 layer forming the Schottky contact. The schematic representation of the multilayered sensor structure is shown in Fig. 1.

The entire device was annealed at 450 °C for 4 h and then at 600 °C for another 2 h to establish the ohmic contact and further heat treatment of the deposited TiO_2 layer in an ambient of air. The surface states and chemical composition of the thin films deposited on SiC was analyzed using XPS using an Al $K\alpha$ X-ray source in an ultrahigh vacuum system (Kratos Analytical Inc., Manchester, UK) with a chamber base pressure of ~ 1.33×10^{-7} Pa. The binding energy (BE) scale was calibrated by measuring reference peaks of Au 4f7/2 (84.0 eV) and of C 1 s (285.0 eV) from the initial contamination of the surface. The Ar^+-ion beam of 2.0 keV energy, rastered over an area of 1 × 1 mm^2, when operated at a current density j = 3 μA/cm^2. The interfaces (Pt/TiO_2 and TiO_2/SiC) of the $Pt/TiO_2/SiC$ in various conditions (as deposited, annealed and tested) were studied using RBS analysis at the Hope College Ion Beam Analysis Laboratory with a 2.91 MeV He^+ ion beam and a beam current of ~15 nA. A Si surface barrier detector was fixed at 162 ° to the beam direction and calibrated with a mixed alpha source. RBS spectra were accumulated up to a total charge of ~ 20 μC. Current–voltage (*I–V*) characteristics were measured using a Keithley 2600 current source meter.

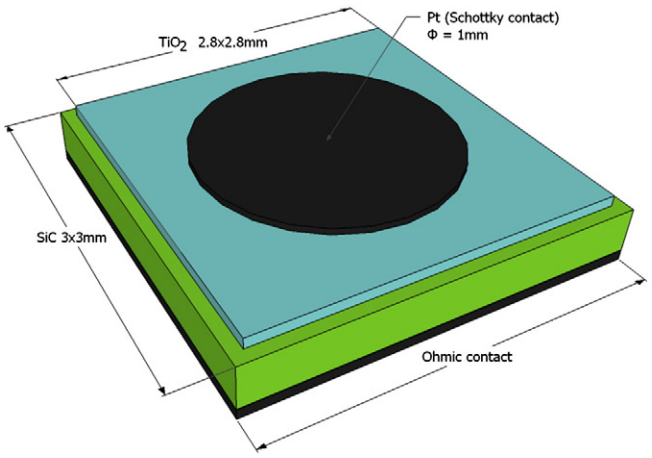

Fig. 1. Schematic configuration of multi-layered sensor structure.

3. Results and discussion

3.1. Electrical-gas sensing characteristics

Fig. 2(a) shows the current–voltage (*I–V*) characteristics of the $Pt/TiO_2/SiC$ sensor at 530 °C when exposed to different hydrogen gas concentrations in synthetic air. The device exhibits not only a consistent lateral shift towards lower voltages when exposed to different hydrogen gas concentrations, but also a change in the slope of the *I–V* curves. Such an observation is typical for devices comprising a semiconducting oxide layer, and unlike those for devices based on insulating oxide layers such as SiO_2.The barrier height at the Pt/TiO_2 interface is assumed to be equal to the difference between the work function of the metal and the electron affinity of the metal oxide semiconductor in air or equilibrium. The work function of the Pt metal is reduced upon exposure to hydrogen, resulting in a lowering of the barrier height, and as a consequence a shift to lower potential in the *I–V* curves. A similar negative shift of the onset potential for $Pd\text{-}TiO_2$ Schottky diodes was proposed [21]. Based on the thermionic field emission conduction mechanism of Schottky diodes [22], the dependence of the effective change in barrier height $\Delta\phi_B$ (at the metal-oxide interface) on the H_2 gas concentration is shown in Fig. 2(b). Each data point was derived using the saturation current obtained by extrapolating the linear portion of the *I–V* curve plotted on a semi-logarithmic scale. The effective change in the barrier height gradually increases, reaching saturation beyond H_2 gas concentrations of 0.5%. This saturation arises when the energy bands at the interface have been completely flattened. The resulting barrier height in the flat band condition is therefore understood as the difference in the semiconductor work function and electron affinity, in the absence of surface states. The $\Delta\phi_b$ value at which complete flattening, and hence response saturation, occurs was found to be 125 meV. When the sensor was exposed to 1% H_2 the barrier height reduced from 1.54 to 1.42 eV. The voltage-time saturation sequence, upon exposure to H_2 gas at 530 °C is shown in Fig. 2(c). The sensor response was measured as a shift in voltage when the device was held at a constant bias current of 9 μA. For hydrogen gas concentrations of 0.125, 0.25 and 0.5%, the corresponding voltage shifts observed were 70, 110 and 160 mV. The detailed dynamic response characteristics to different concentration of hydrogen and propene gases over a temperature range of 150 to 650 °C is presented elsewhere [18].

3.2. Material characterization

The surface and interfacial material properties of the devices prior and post exposure to hydrogen gas were investigated using XPS and RBS techniques. Firstly, the surface chemical state of the TiO_2 thin films deposited on SiC was examined by XPS. Fig. 3(a) shows the XPS survey spectrum of a TiO_2 thin film, revealing the presence of Ti, O and some traces of C. Fig. 3(b) shows the photoelectron spectra of Ti 2p. The spin–orbit components ($2p_{3/2}$ and $2p_{1/2}$) of the Ti_{2p} peak are distinctly indicated at approximately 458.9 and 464.4 eV, corresponding to Ti^{4+} in a tetragonal structure, with a separation of 5.5 eV between the two peaks. This is a typical characteristic of Ti^{4+} state in TiO_2 [23,24]. The O 1 s spectrum as shown in Fig. 3(c) was de-convoluted into two peaks at 530.1 and 532.1 eV which can be attributed to the lattice oxygen Ti-O in TiO_2 and hydroxyl groups respectively, chemisorbed on the surface of the samples [25,26]. TiO_2 surfaces have been well known for chemisorption, where surface defect sites (oxygen vacancies) act as electron donors and are specific sites for hydrogen adsorption. Chemisorption of hydrogen forms ionic titanium hydride bonds $Ti^{4+}\text{-}H^-$ after H_2 dissociative adsorption at these defect sites [27]. This leads us to believe that the selected gas

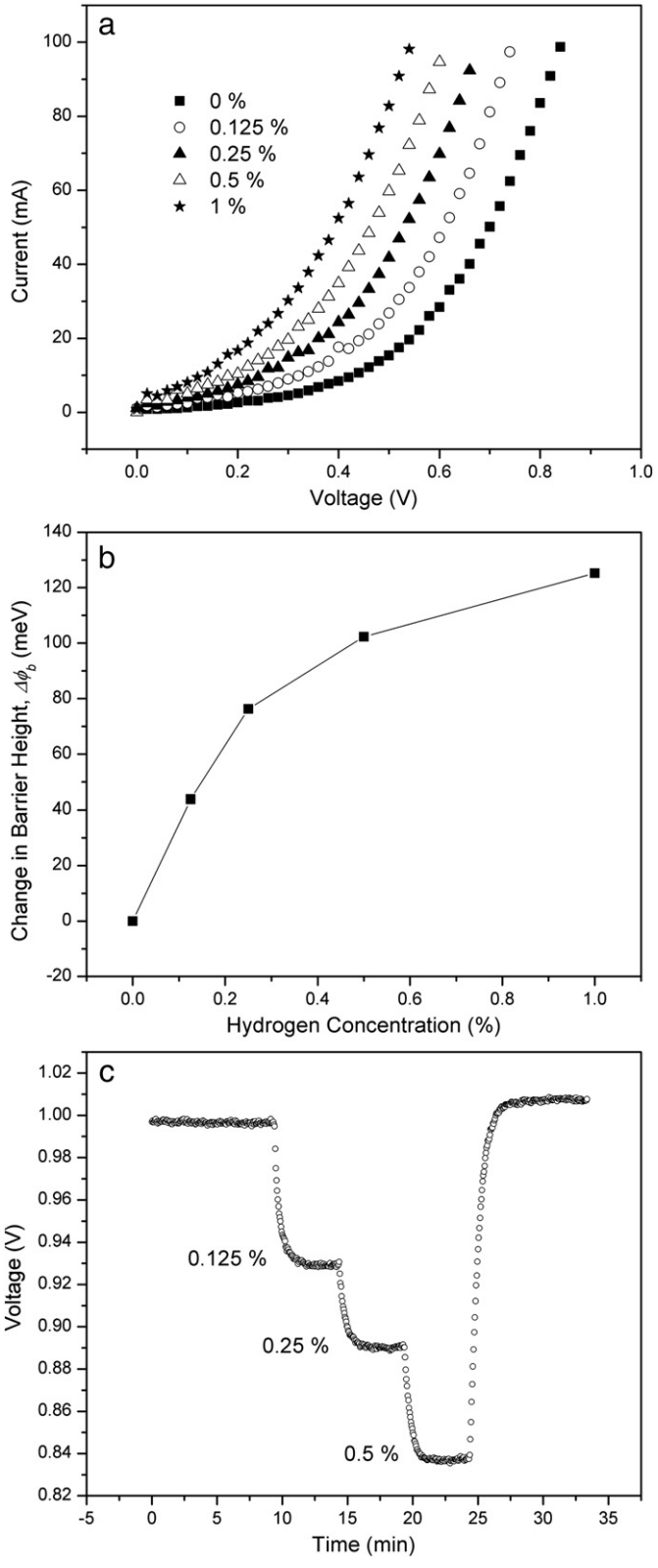

Fig. 2. (a) Current–voltage (I–V) characteristics of the Pt/TiO_2/SiC sensor at 530 °C when exposed to different hydrogen gas concentrations in synthetic air, (b) Relationship between the effective change in the barrier height ($\Delta\phi_b$) and the H_2 gas concentration, (c) Hydrogen saturation sequence of the Pt/TiO_2/SiC device at 530 °C.

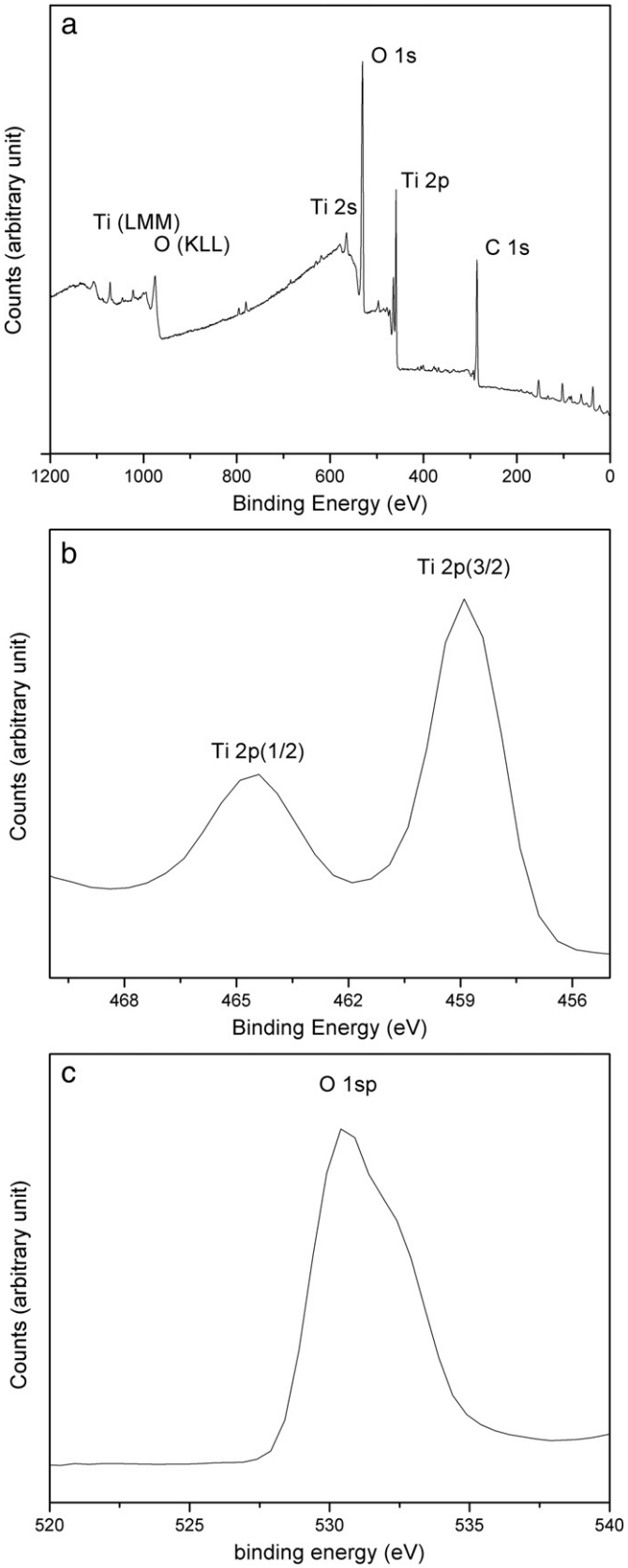

Fig. 3. (a) XPS survey spectrum of TiO_2 thin film deposited on SiC, (b) Photoelectron spectra of Ti 2p region, (c) Photoelectron spectra of O 1 s region.

sensitive layer TiO_2, plays an important role in the gas response mechanism.

For reproducible and reliable operation of such Pt/TiO_2/SiC structures, the stability of the metal/oxide and the oxide/semiconductor

interfaces are critical. Inter-diffusion between different layers at elevated temperatures does significantly affect the sensor performance. In this study, the thermal stability of the $Pt/TiO_2/SiC$ device with respect to inter-diffusion of different elements at the interfaces of Pt/TiO_2 and TiO_2/SiC was characterized using RBS. The composition of the as-fabricated sensing structure is used as a reference for comparing the changes in composition after annealing and testing. The simulation software RUMP [28] was used to fit the experimental data presented with yield normalized to the incident beam current to determine the thickness and composition of different layers in the proposed $Pt/TiO_2/SiC$ structure. From the simulated RBS data, the thickness of Pt and TiO_2 were found to be approximately 130 and 45 nm, respectively. RUMP analysis indicated that the Ti to O ratio of these films is around 1:2. The results show that the TiO_2 films were of near stoichiometric composition.

The RBS spectrum of a $Pt/TiO_2/SiC$ sample in different conditions is shown in Fig. 4. The sharp edges of the Pt signal in the backscattering spectrum of the as-deposited sample in Fig. 4(a), indicates a pure Pt top layer with a sharp interface with TiO_2 layer. Similarly interface between TiO_2 and SiC layers also didn't show any significant inter-diffusion between the film and substrate in the as-deposited condition. Annealing the $Pt/TiO_2/SiC$ samples at 600 °C for 5 h showed an observable variation at the interface between the Pt and TiO_2 layers. This is evident from the change at the trailing edge of the Pt signal at channel number of around 820. Apart from that, no significant change in the spectrum between the as deposited and annealed sample is observed. The testing of the $Pt/TiO_2/SiC$ device consists of cycling the sensor under different thermal conditions ranging from room temperature up to 650 °C for several days and exposing the device to different gas concentrations (0–1%) of hydrogen, oxygen and propene for a maximum of 30 min per cycle. The RBS spectrum of the tested sample featured a further broadening of the curve at Pt/TiO_2 interface, whereas the TiO_2/SiC interface showed same variation as that of previously annealed sample. This can be observed at a channel number of around 500, which represents the Si edge. However, this change in the interface seems to have confined to a very small thickness of few nanometers. As the overall observed inter-diffusion is minimal, it would have helped in stabilizing the sensor performance to achieve good repeatability even after a number of cycles of operation. Roy et al., [29] studied the thermal effects on the interface of Pd/β -SiC devices, where annealing at 800 °C caused deterioration of the interface due to substantial inter-diffusion at the Pd and β-SiC interface. Similarly Chen et al., compared the interfacial properties of Pd/SiC and $Pd/SiO_2/SiC$ devices using Auger electron spectroscopy [30]. In that particular study, the presence of the SiO_2 barrier layer might have helped in preventing the inter-diffusion between Pd and the SiC substrate. However changes in the surface properties of the Pd layer due to surface diffusion lead to changes in the device's sensitivity to hydrogen. In our case the TiO_2 layer prevents the Si and C atoms from out-diffusion towards the surface and acts as a diffusion barrier for the Pt thin catalytic layer. This certainly helps in understanding the sensing performance of the fabricated structure in terms of long-term stability.

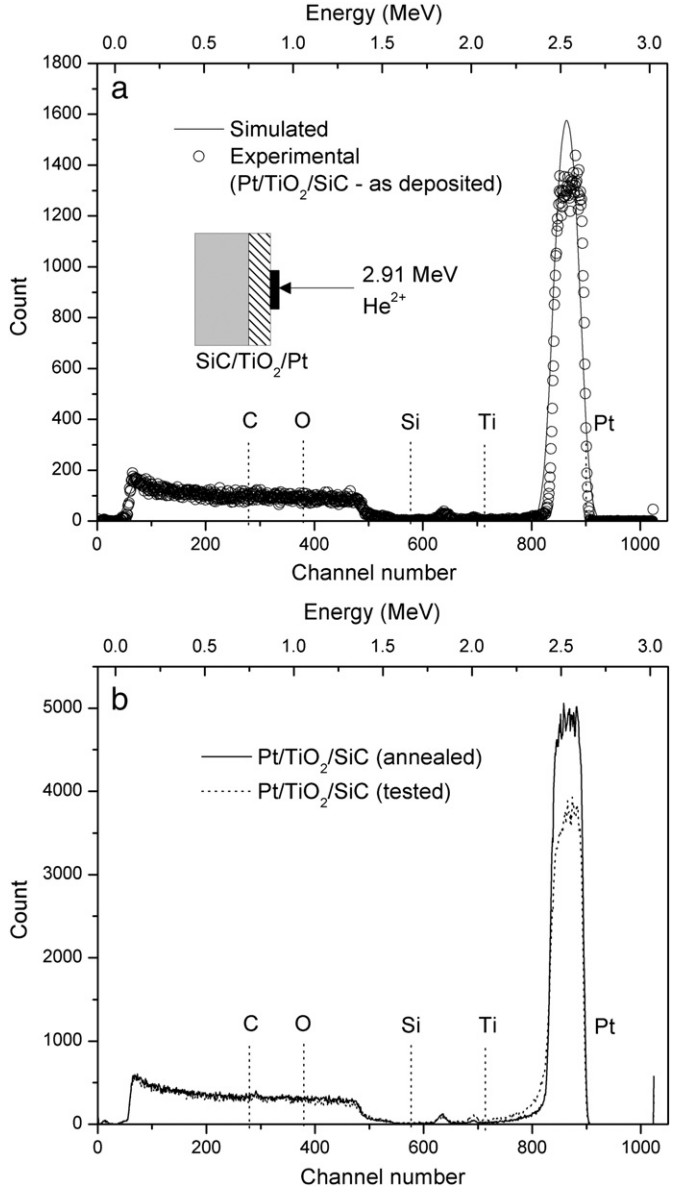

Fig. 4. RBS spectra of $Pt/TiO_2/SiC$ multilayer structure in different conditions (a) the experimental spectrum for as-deposited film overlapped with the simulated spectrum (b) Experimental spectra for annealed and tested film structures.

4. Conclusion

High temperature gas sensing performance of $Pt/TiO_2/SiC$ based Metal Reactive Oxide Silicon Carbide (MORSiC) devices has been investigated. A shift in the *I–V* characteristics of the $Pt/TiO_2/SiC$ sensor towards lower potential upon exposure to H_2 gas indicates a reduction in the metal-oxide interface barrier height, arising from the flattening of the energy bands at the interface. The effective change in barrier height $\Delta\varphi_b$ for 1% H_2 in air was found to be 125 meV. The RBS analysis of the devices after annealing and testing revealed minimal inter-diffusion at the Pt/TiO_2 and TiO_2/SiC interfaces. The presence of TiO_2 layer in this structure might have helped in arresting/minimizing cross-diffusion within these layers, and it is believed that this serves to aid achieving stable sensing performance of the sensor after repeated cycles of operation.

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